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FILM PROPERTIES USING METAL SALTS WASHING FOR PEROVSKITE SOLAR CELLS

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Abstract

Perovskite Solar Cell (PSC) is a third-generation photovoltaic device known for its rapid improvement in efficiency levels over the past decade. Moreover, the added benefits of abundant sourcing of raw materials, uncomplicated fabrication process, organic and inorganic device materials, and tuneable bandgaps make this technology a sustainable energy alternative. However, the efficiency values of these devices are subjected to variation depending on factors such as material compatibility, environmental conditions, energy band alignment of device components and stability characteristics to extrinsic and intrinsic factors. One such vital intrinsic factor is film morphology, homogenous and superior film quality formation and pinhole and trap-free films. In this study, we have investigated the formation of perovskite films on a qualitative basis using metal chloride washing of salts such as Erbium, Antimony, Cadmium and Chromium Chloride. The study aims to analyse the difference in film formation with various metal chloride washing and how this could potentially impact or contribute to photovoltaic performance if the devices are fabricated.

Keywords

Perovskites, Solar cells, Film formation, Solar energy, Doping

1. INTRODUCTION

The world's power demands are on an ever-increasing rise with no foreseeable decrease in the long run. The power demands are being met by non-renewable energy sources such as petroleum-based or derived products. It is important to note that these energy sources have a drastic impact on workers' health levels and the environment as they release an intense amount of greenhouse gases. This very need calls researchers and scientists to explore renewable energy sources, more particularly, emerging technologies in the solar energy space. One such revolutionising piece of technology is the perovskite solar cell (PSC).

PSCs have received much attention, extensive research and a fair number of resources in order for them to escalate appropriately in terms of efficiency, stability and material aspects. However, amongst these factors, the need to improve device stability and efficiency is under constant innovation. One needs to develop devices with a possible increase in efficiency that can compete with other energy technologies whilst being extremely stable.

The key intrinsic factor in developing such devices has a smooth, homogeneous and uniform perovskite layer. A film following these properties will improve device performance by allowing smooth transfer of charges across the bulk surface and interfacial components and reducing the number of trap density states and pinholes. This eventually reduces the number of charge recombinations, resulting in higher short-circuit current (J_{sc}) values. A smooth film also indicates a higher degree of crystallinity, improved surface coverage and more excellent wettability. The perovskite growing process should be conducted under-regulated and under favourable conditions.

In this experiment, we looked into how perovskite film formation is affected by washing various metal chlorides. We have used Erbium, Antimony, Cadmium and Chromium Chloride as the appropriate metal salts. The films formed in this case have been of exceptional quality, with specific counterparts being better than the other.

2. MATERIALS

The chemical requirements for this experiment are Indium-doped Tin Oxide glasses (ITO), PEDOT:PSS (P VP Al 4083), IPA, Lead Iodide (PbI_2), Methylammonium iodide (CH_3NH_3I (MAI)). In addition to this, commercial-grade (Sigma) Erbium Chloride, Antimony Chloride, Cadmium Chloride and Chromium Chloride ($ErCl_3$, $SbCl_3$, $CdCl_2$ and $CrCl_3$) metal salts are required. The perovskite precursor solution was prepared in a 1.4:1.4 molar ratio of MAI and PbI_2, dissolved in Gamma-Butyrolactone (GBL). The solution was stirred continuously overnight at 65 ^{o}C, and then filtered using a 0.45 µm PVDF syringe filter before depositing on the substrate.

3. FABRICATION

The fabrication was conducted in ambient conditions (relative humidity 50-60%, temperature 20 ^{o}C). The first step involves cleaning the ITO substrate with acetone, toluene and ethanol. The substrates are subjected to an Ultrasonic-assisted cleaning with acetone and isopropyl alcohol (IPA). The substrates are dried, and the HTM (PEDOT:PSS) is spin-coated at 2000 rpm for 50 s. The substrate is thermally annealed at 135 ^{o}C for 10 mins. Before spin-coating the perovskite layer, it is necessary that the perovskite solution and the substrate are sufficiently hot (~ 95 ^{o}C). This ensures a homogeneous film spread across the substrate and reduces pinhole formation. The perovskite layer is spin-coated at 2000 rpm for 10 s and 4000 rpm for 20 s. At the twenty-eighth second, anti-solvent washing is carried out.

The solution used to perform the anti-solvent washing was metal chloride salts dissolved in toluene. 1 mg/ml of metal chloride in toluene was subjected to slight heating (~ 40 ^{o}C) and Ultrasonic-assisted dissolving mechanisms. The solutions were allowed to dissolve overnight. The cooled-down solutions were then filtered using a 0.45 µm PVDF syringe filter. The obtained substrates are thermally annealed at 100 ^{o}C for 20 mins, and the films are qualitatively studied.

4. RESULTS AND DISCUSSION

The generalised structure of the various films using metal salt washing is shown in figure 1.

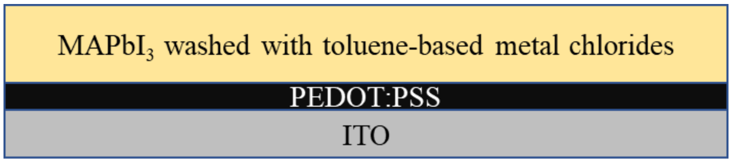

Figure 1. Half-device structure

Erbium chloride-based films showed an improved device film quality than the reference device. This result can be verified by the study by Rong et al. [1]. The study implies how Erbium-doped MAPbI$_3$ shows a reduction in trap states by 37%. Moreover, the washing of Erbium not only reduces the number of defects on the surface but contributes to a lower acceptor level which is crucial for effective photovoltaic performance. Through further tests, one can conclude that conductivity and carrier mobility is improved, and optimised photovoltaic performance is observed. Rong's photoluminescence (PL) studies showed that incorporating Er in PSCs improved the external quantum efficiencies (EQE) compared to the reference devices.

Zhu and coworkers showed how modifying films using Er could produce films with excellent morphology, reasonable crystal size and cubic shape [2]. Additionally, tuning the perovskite film using Er can vary the tolerance factor towards a more stable and valid value. The PL analysis show reduced radiative and non-radiative charge recombination. Moreover, the Cl^- ions present along with I^- ions effectively contribute to the absorption and emission spectra of the fabricated device. There is a notable decrease in decay constants, which contributes to the operation of the film. The washing or doping of Er can not just improve the optoelectronic properties of the produced film/device but rather facilitates the application of the device to a broader scope of fields.

Antimony Chloride-based films are regarded as developing a new era of perovskites, known as wide-bandgap perovskites. In our experiment, we observed that Sb-based perovskites showed a different colour (orangish-yellow) than their other counterparts. This can be attributed to the variation in bandgap values and perovskite formation ability. Zhang's works suggest that Sb-based perovskites create a favourable absorption response compared to the reference device [3]. Moreover, the presence of Sb increases the J_{sc} value of the fabricated device to produce high-efficiency devices. With a notable increase in J_{sc} values, there is a corresponding increase in EQE values. In some cases, when there is a sufficient amount of Sb present in the perovskite, the absorption shifts to lower regions of wavelength, which is essential as broad absorption properties are observed.

Zhang's works show that the EQE value is more excellent than 80% for Sb-based films. The Sb includes a shift in conduction band values, which contributes to an increase in V_{oc} values. An increase in Sb content can lead to a reduction in carrier lifetime due to increased defects. It is also proved that Sb-based perovskites have greater electron diffusion length values, facilitating improved charge collection and transportation. Using techniques like antisolvent washing or doping, one must be cautious while incorporating Sb into perovskites.

Moreover, in some non-ideal cases, Sb also generates certain impurity, trap and defect states to disrupt the crystalline quality of the perovskite film produced. Xiang's works suggest that a moderate amount of Sb can improve the morphology as it reduces the grain boundaries [4]. Liu's works depict that the addition of Sb produces a compact, flat and increased grain size film, with an improvement to film crystallinity. There is also a significant increase in PL spectra which is higher than the reference device. This work showed a remarkably observed decrease in charge recombination as the recombination resistance (R_{rec}) value increased. The stability of Sb-modified devices is investigated, and it is observed that such devices depict improved stability in ambient atmosphere, high water and thermal environments. The perovskite degradation was much slower in Sb-infused perovskites as the presence of intrinsic ionic-based defects was significantly reduced.

Table 1 highlights device examples with remarkable performances using Er, Sb, Cd and Cr metals to produce high-efficiency devices.

Table 1. Notable performances of PSCs with metals

Metal/Perovskite	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	**PCE (%)**	**Ref**
Er/$CsPbIBr_2$	1.34	12.36	11.61	[8]
Sb/$MAPbI_3$	1.13	16.29	12.8	[9]
Cd/$MAPbI_3$	1.04	20.76	14.68	[5]
Cr/$MAPbI_3$	1.101	26.31	22.35	[10]

Cadmium Chloride is a possible candidate for developing high-performance and desirable PSCs with scalable and flexible applications. Tong and coworkers studied the doping of Cd in perovskites and its effect on optoelectronic properties [5]. The film's morphology is found to have a reduced number of pinholes than the reference device. The film's uniform surface coverage aids charge transport and significantly reduces charge recombination. It has also been proven that including Cd either by doping, washing, or molecular engineering can even tune the morphology of the perovskite films by increasing the grain size. A high-quality film is produced with a surface roughness lower than the reference device. Wang's research suggests how Cd's incorporation can improve film crystallinity and increase the tolerance factor value, thus improving the stability of the perovskite structure [6]. The addition of Cd produces a uniform film with a larger grain size free of pinholes, along with a perpendicular grain arrangement, possibly decreasing non-radiative recombination.

However, it is essential to note that increasing Cd film thickness/content can increase the series resistance. This consequently decreases the photovoltaic performance of the fabricated device. An optimum quantity of Cd is required for perovskite incorporation; otherwise, there can be a chemical reaction between the perovskite and $CdCl_2$, which eventually degrades the perovskite. Tong's study reports how CdS degrades the perovskite in three steps if not deposited with care. The higher film crystallinity corresponds to an increase in absorption range higher than the reference devices. Cd inclusion also lowers the conduction band, which allows a smoother flow of electrons. The PL spectra of the fabricated devices indicate the reduced radiative charge recombination with a well-defined increase in carrier lifetime. The optical response for Cd-modified films is much higher than the reference films. This property makes it suitable for photoelectric conversion applications. The reduced charge recombination will account for an increase in R_{rec} values. At the same time, one needs to be cautious about the increase in series resistance (R_s) values. The reduced recombination rate can be related to the decay and carrier lifetime, shown through Chen's works [7]. A film with a long carrier lifetime shows improved film quality and lower trap/defect states. Cd-based perovskite films showed improved stability in an inert atmosphere but succumbed severely to moisture-intensive environments.

Chromium Chloride-based perovskites have been famous mainly for their highly stable nature and improved photovoltaic response. These properties make it a perfect candidate for photoelectric-based devices. Cr-modified perovskites maintain a cubic phase, with dimensions varying with Cr concentration. Zhou et al. showed how Cr-infused perovskites could passivate the perovskite defects entirely [10]. Density Functional Theory (DFT) calculations show that there are no primary or secondary defects present other than Cr-induced defects.

Moreover, substituting Pb with Cr shifted the absorption characteristics to shorter wavelengths. The improved passivation of Cr consequently increases the luminescence effect. The reduction in defects also accounts for a decrease in radiative and non-radiative recombination, which also implies an increase in decay lifetime.

Zhou's work further showed how Cr-doping in perovskites could improve the stability of the fabricated device, with more excellent resistance to air, water and UV-light exposure. The increase in PL stability is also regarded as improving the structural stability of the perovskite crystal structure. The addition of Cr to perovskites accounts for a broader wavelength absorption. This nature accounts for the increased value in J_{sc} and incident photon to current efficiency (IPCE). It is crucial to consider the thickness of the Cr layer, especially while adding an interlayer or washing, as it can contribute to R_s and thus impact photovoltaic performance. García et al. showed how adding Cr shifted the conduction band (CB) and valence band (VB). This shift improved sunlight absorption and facilitated charge transition efficiently to produce a highly effective photovoltaic device [11].

Figure 2 shows the various devices fabricated in our work using metal chloride washing. We studied the film properties qualitatively.

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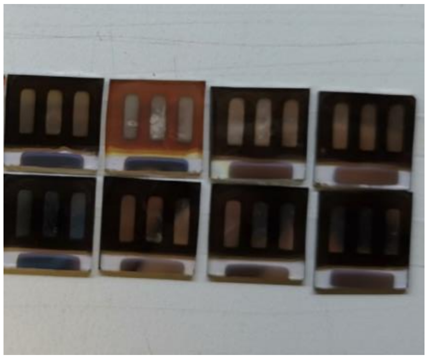

Figure 2. Fabricated devices using metal chloride washing

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